Submitted to Fusion Technology

SEARCH FOR ^{3}He and ^{4}He IN ARATA-STYLE PALLADIUM CATHODES I: A NEGATIVE RESULT

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Number of pages = 15
Number of tables = 2
Number of figures = 3

ABSTRACT

^{3}He and ^{4}He concentrations in 2-6 mg samples of palladium-black from the interior of Arata-style cathodes were investigated using a tungsten wire furnace on-line to an ultra-high sensitivity static mass spectrometer. The detection limit of the mass spectrometer was about 10^4 atoms ^{3}He and 10^8 atoms ^{4}He, and the mass resolution of 1 part in 620 was sufficient to cleanly resolve ^{3}He from H_3 and HD. Three specimens of palladium black (A, B, and C) were from hollow Pd cathodes which had generated excess heat in D_2O electrolysis experiments carried out by Arata and Zhang in their laboratory. One specimen of Pd-black (D) had not been used in any electrolysis experiment. A total of twelve samples, three from each specimen, were analyzed. ^{3}He and ^{4}He concentrations were variable as if due to sample inhomogeneity. Two samples (C-1 and B-1) showed apparent ^{4}He of 4.4×10^9 atoms/mg and 6.6×10^9 atoms/mg respectively, and three (A-3, B-2, and D-3) showed excess ^{3}He from 77 to 1096×10^3 atoms/mg relative to the atmospheric ^{3}He/^{4}He ratio. Seven samples showed no apparent excess of ^{3}He or ^{4}He. Five samples of the aluminum foil used to wrap Pd-black samples were also analyzed and gave mean values of $13\pm18\times10^3$ atoms/mg and $1.50\pm0.66\times10^9$ atoms/mg for ^{3}He and ^{4}He respectively. The values for Al and Pd-black are comparable to the 1978 results of Mamyrin, Khabarin, and Yudenich who examined helium isotopes in many ordinary metals and other materials including Al and Pd. However, at present there is no evidence for the very much larger concentrations (10^{16}-10^{17} atoms/mg) of ^{3}He and ^{4}He which Arata and Zhang claim to have detected in similar specimens of Pd-black from Pd cathodes subjected to D_2O electrolysis.

INTRODUCTION

In 1989, Fleischmann and Pons (1) reported that they had achieved excess heat production during heavy water electrolysis using palladium cathodes. These workers proposed that their observations were evidence for fusion of deuterium nuclei in palladium near room temperature. Since then, many attempts have been made to repeat the original observations and extend them to other possible fingerprints of D-D nuclear fusion. Some of these attempts have claimed success, and some have reported negative results. The reader is referred to reviews by Storms (2) and Nagel (3) and to several books on so-called "cold fusion" with differing points of view including those by Mallove (4), Taubes (5), and Huizenga (6).

In 1995, Arata and Zhang (7) reported that they had detected large amounts of ^{4}He, 10^{20}-10^{21} atoms/cm^3, equivalent to approx 10^{16}-10^{17} atoms/mg, in Pd-black powder sealed under vacuum inside Pd cathodes during D_2O electrolysis. These are extraordinarily large amounts of helium from the point of view of a present-day noble gas mass spectroscopist. Arata and Zhang's results were obtained by heating the Pd-black powder to 1500 K in a vacuum system attached to a statically-operated quadrupole-type mass spectrometer, and were stated to be "fully repeatable". In a following paper, Arata and Zhang (8) reported that they had confirmed the ^{4}He observation, and also had detected ^{3}He, with ^{3}He/^{4}He ~ 0.25. Helium isotopes were not detected in comparable electrolysis experiments using H_2O. It should be noted that helium isotope assay was carried out in an unusual way. Two quadrupole mass spectrometers were used, one of which was tuned to mass 4 with sufficient resolution (~ 1 part in 200) to separate ^{4}He from D_2, and the other was tuned to mass 3 at similar resolution. Because such mass resolution is insufficient to resolve ^{3}He from the species HD

and H_3, the contribution of ^3He was estimated from examination of plots of ion current intensity versus electron ionizing voltage. In subsequent papers, Arata and Zhang (9, 10, 11) reported additional data obtained with their ^3He detection technique and other features in more detail, and restated their claims regarding excess ^3He and ^4He. They also noted that trapped helium was released from Pd-black only above about 1000 ^0C. In a more recent paper, Arata and Zhang(12) described additional measurements of ^3He and ^4He in the gas phase sample produced during electrolysis (~2000 hrs) of hollow Pd cathodes filled with Pd-black. The total observed ^4He was about 5.7×10^{15} atoms and no detectable ^3He was present. Arata and Zhang stated that "the amount of ^4He gas detected in the present experiment, however, is at least 20 times larger than the previous one observed in heating remnant Pd fine powders". Subsequently, the authors stated "The amount of gaseous ^4He is about two order larger than that found previously from heated Pd powders" (12). It may be possible to reconcile these two statements if the former refers only to ^4He in the gas phase, and that the latter refers to ^4He in the gas phase plus that released by heating the Pd-black. However, it does not seem possible to reconcile the above two statements with the stated total ^4He amount of 5.7×10^{15} atoms and that of 10^{20}-10^{21} atoms given previously (7).

In spite of the quantitative difficulties described above, the implications of the ^3He and ^4He observations of Arata and Zhang are of profound significance. It was decided that helium isotope analyses on their Pd-powders should be carried out using different measurement techniques. In this connection, Professors Arata and Zhang were generous enough to give four samples of Pd-black (three of which had undergone D_2O electrolysis and generated significant excess heat) to Mr. R. George who kindly provided them to me.

EXPERIMENTAL METHODS

Samples of Pd-black (2-6 mg) were placed in 1.0 cm^2 pieces of aluminum foil which were folded several times and then placed in a tungsten coil furnace described previously (13). The coil was attached to a variable voltage supply and heated to approx 2300 ^{0}C resulting in evaporation of the Al to form a "mirror" on the inside wall of the furnace followed by evaporation of the Pd-black. The temperature of 2300 ^{0}C was held for about 30s. In some cases, the tungsten coil broke near the end of the heating period. Examination of the coils and the interior of the furnace after heating showed that vaporization of aluminum was always complete and vaporization of Pd samples was always better than 90%. The tungsten coil was outgassed at about 2300 ^{0}C for 2 min. prior to loading the aluminum-wrapped sample. A pump time of at least 12 hrs. was necessary to achieve a sufficiently low helium line blank. Helium in the line blank was mainly due to release of atmospheric helium from the pyrex glass envelope of the furnace.

The furnace container was attached to the sample line of the helium isotope mass spectrometer as described previously (13) with minor modifications. The mass spectrometer was employed essentially as a peak height manometer calibrated with helium from air aliquots of volume 0.008 cc STP containing 1.1×10^{12} atoms ^{4}He and 1.5×10^6 atoms ^{3}He. A daily measurement run consisted of analysis of an air aliquot followed by two line blanks; then the sample was analyzed and the series was completed by analysis of a third line blank sometimes followed by a second air aliquot. During this series of measurements over a 2-month period, line blanks steadily decreased from 8×10^8 atoms to 4×10^8 atoms ^{4}He with ^{3}He/^{4}He equal to the atmospheric ratio of 1.38×10^{-6} ($\pm$ 30%). Several blank runs were carried out wherein the tungsten coil alone was heated to 2300 ^{0}C for 30- 60 s. Many other blanks were carried out by vaporizing 0.1-2.0 cm^2 aluminum foil pieces alone

and with loadings of 1-5 mg pieces cut from Pd wire. Some blanks were run by vaporizing 4-8 mg pieces of ordinary palladium wire without aluminum wrapping.

The helium isotope mass spectrometer is a 10 in. radius branch-tube statically operated instrument designed and constructed with a low internal volume for high sensitivity (14). ^{3}He is detected with a Johnson MM-1 electron multiplier and ^{4}He is detected simultaneously with a Faraday cup. Source and collector slit widths of 0.1 and 0.3 mm allow a mass resolution of 1 part in 620 which ensures that under normal conditions, ^{3}He is cleanly resolved from H_3 and HD. Figure 1 is an accurate tracing of a magnet scan of mass 3 ion currents recorded for a standard air aliquot of 0.008 cc STP and shows that the ^{3}He measurements are not significantly affected by the background hydrogen peaks at mass 3.

RESULTS AND DISCUSSION

Helium in the aluminum foil

Results for five samples of aluminum foil are given in Table I. The quoted uncertainties are estimates which include random and systematic components at the level of one standard deviation. The results are also plotted in Figure 2. Two samples contain definite excess ^{3}He, relative to the atmospheric ^{3}He/^{4}He line shown in the diagram. All samples appear to contain traces of ^{4}He which are probably due to micro bubbles of air trapped in the aluminum during manufacture. However, excess ^{3}He in the two anomalous samples cannot be explained in this way, and must be due to decay of man-made tritium, or to some other mechanism. Be that as it may, the mean values given in Table

I were used to subtract the Al foil contribution from helium isotope results for Al-wrapped Pd samples.

Helium in the Palladium-Black

Although the set of twelve samples from the four specimens A,B,C, and D is admittedly very small, it would appear that the helium isotope results given in Table II and Figure 3 are in serious disagreement with the very much higher values claimed by Arata and Zhang for similar specimens (7, 8, 9, 10, 11, 12). In this connection, Professor Arata kindly transmitted details of excess heat production in his laboratory for the three specimens A, B, and C (15). Specimen A had generated approx 70 MJ (~20 KJ/hr for 3500 hrs), specimen B had generated about 100 MJ (~25 KJ/hr for 4000 hrs), and specimen C had generated a comparable amount of heat for a similar time as for A and B. These amounts may be compared to the value of about 100 MJ for several thousand hours given by Arata and Zhang (7). As mentioned previously, one sample analyzed in this work (D-3) was a specimen of Pd-black that had never been used in an electrolysis experiment.

Helium in Other Materials

Mamyrin et al. (16) have found that ^{3}He is distributed in "patchy" fashion in a large number of metals (including Al and Pd) and other materials, whereas ^{4}He is fairly evenly distributed. These authors gave detailed results (in a diagram) only for nickel foil in which they found ^{3}He concentrations of 7×10^3 to 2×10^6 atoms/mg in 0.55 g pieces, with large variations seen even in adjacent pieces. It will be noted that these values are quite similar to those found in this work for the Al foil and Pd-black specimens. Mamyrin et al. suggested that excess ^{3}He was associated with

hydrogen, i.e. due to the decay of ^3H, because of the patchy distribution and the fact that ^3He was released from Ni foil at relatively low temperatures, 100-500 ^0C. They also suggested that because the deduced $^3H/^1H$ ratio of~ 10^{-9} in aluminum samples exceeded the expected $^3H/^1H$ ratio in ambient media (assumed to be H_2O) by 6-8 orders of magnitude, the ^3H was formed by fusion of deuterium nuclei catalyzed by some unknown particle in a similar way to that caused by negative muons. Clarke and Clarke (13) subsequently pointed out that a more plausible source of tritium in metals and other materials was atmospheric hydrogen. The worldwide average $^3H/^1H$ ratio in atmospheric hydrogen gas from 1970 to 1974 was ~2 $\times 10^{-12}$ (15), several orders of magnitude higher than in ambient H_2O at that time, and indeed may have been much higher that 2 $\times 10^{-12}$ near industrial releases of tritium or thermonuclear testing in the USSR. It was opined that the "cold fusion" origin via ^3H for the sporadic amounts of excess ^3He observed by Mamyrin et al. should not be taken seriously unless contamination by man-made tritium is ruled out.

Summary

These measurements have shown that:

1. Variable concentrations are found for ^3He trapped in some samples of Al and Pd-black. These anomalous amounts are due to sporadic contamination by man-made tritium or to some other unknown mechanism. Some samples appear to contain traces of ^4He of atmospheric origin.

2. For the three Pd-black specimens employed by Arata and Zhang in D_2O electrolysis experiments, there are seriously large discrepancies between the present results and the much higher concentrations of ^3He and ^4He observed by Arata and Zhang in similar specimens. The discrepancy factor for ^3He is at least 10^9, and the discrepancy factor for ^4He is at least 10^6.

ACKNOWLEDGEMENTS

I wish to thank Y. Arata and Y.-C. Zhang for making their palladium-black samples available and R. George for sending these samples to me. I also grateful to M.C.H. McKubre, and R.H. Tomlinson for helpful discussions and comments. This work was supported in part by a grant from the Natural Sciences and Engineering Research Council of Canada.

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TABLE I

Helium Isotopes in Aluminum Foil

Mass, mg	^{4}He Atoms/mg[a] ($\times 10^9$)	^{3}He Atoms/mg[a] ($\times 10^3$)
4.38	1.55 ± 0.34	3.3 ± 2.7
4.45	2.06 ± 0.05	6.0 ± 3.1
8.83	0.39 ± 0.03	9.2 ± 1.9
4.23	1.59 ± 0.10	45.1 ± 4.8
4.40	1.91 ± 0.05	3.0 ± 2.4
Mean	1.50 ± 0.66	13.3 ± 18.0

[a]Uncertainties are estimates of random and systematic errors at a level of one standard deviation.

TABLE II

Helium Isotopes in Pd-black from Arata-style Pd Cathodes

Sample	Mass, mg	^{4}He Atoms/mg[a] ($\times 10^9$)	^{3}He Atoms/mg[a] ($\times 10^3$)
A-2	3.69	-0.1 ± 0.8	-5 ± 22
A-3	4.90	-0.1 ± 0.8	1096 ± 21
A-4	1.74	0.4 ± 0.6	12 ± 44
B-1	3.28	6.6 ± 1.0	7 ± 24
B-2	5.01	1.2 ± 0.6	77 ± 16
B-3	4.84	0.7 ± 0.6	-7 ± 17
C-1	3.70	4.4 ± 0.8	-6 ± 22
C-2	3.90	-0.4 ± 0.7	-8 ± 20
C-3	5.69	0.1 ± 0.5	-2 ± 14
D-1	2.66	0.9 ± 1.1	-16 ± 30
D-2	5.89	1.1 ± 0.5	-6 ± 14
D-3	4.89	0.6 ± 0.6	366 ± 17

[a]Uncertainties are estimates of random and systematic errors at a level of one standard deviation.

FIGURE CAPTIONS

Figure 1. Mass spectrometer magnet scan trace. ^{3}He is from helium in a 0.008 cc STP air aliquot. Spikes to the left of the ^{3}He peak are due to electrometer scale switching. HD and H_3 are partially resolved instrumental background peaks.

Figure 2. ^{3}He and ^{4}He concentrations in samples of the aluminum foil used to wrap Pd-black samples.

Figure 3. ^{3}He and ^{4}He concentrations in twelve samples of Pd-black.

Figure 1. Mass spectrometer magnet scan trace. ^{3}He is from helium in a 0.008 cc STP air aliquot. Spikes to the left of the ^{3}He peak are due to electrometer scale switching. HD and H_3 are partially resolved instrumental background peaks.

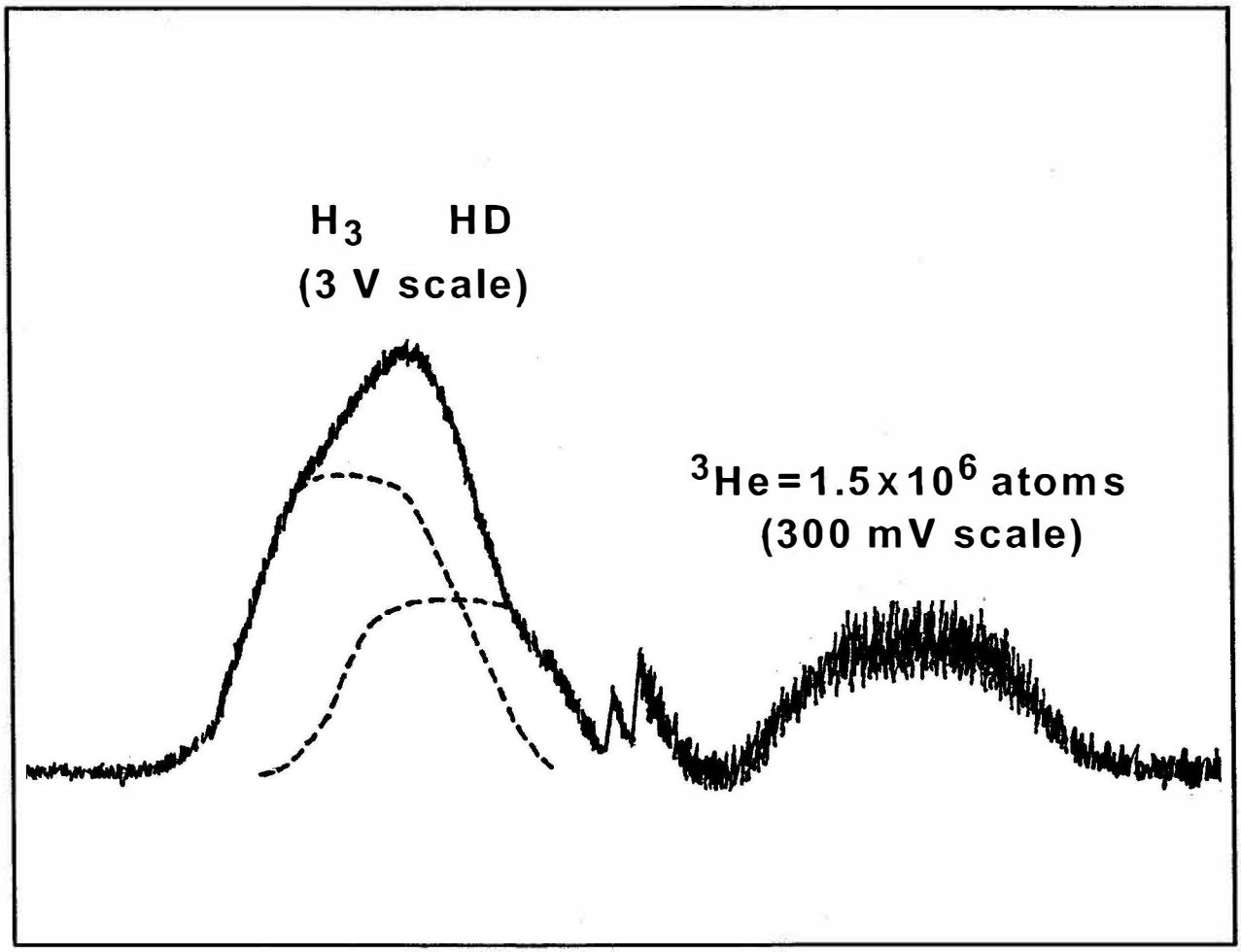

Figure 2. ^{3}He and ^{4}He concentrations in samples of the aluminum foil used to wrap Pd-black samples.

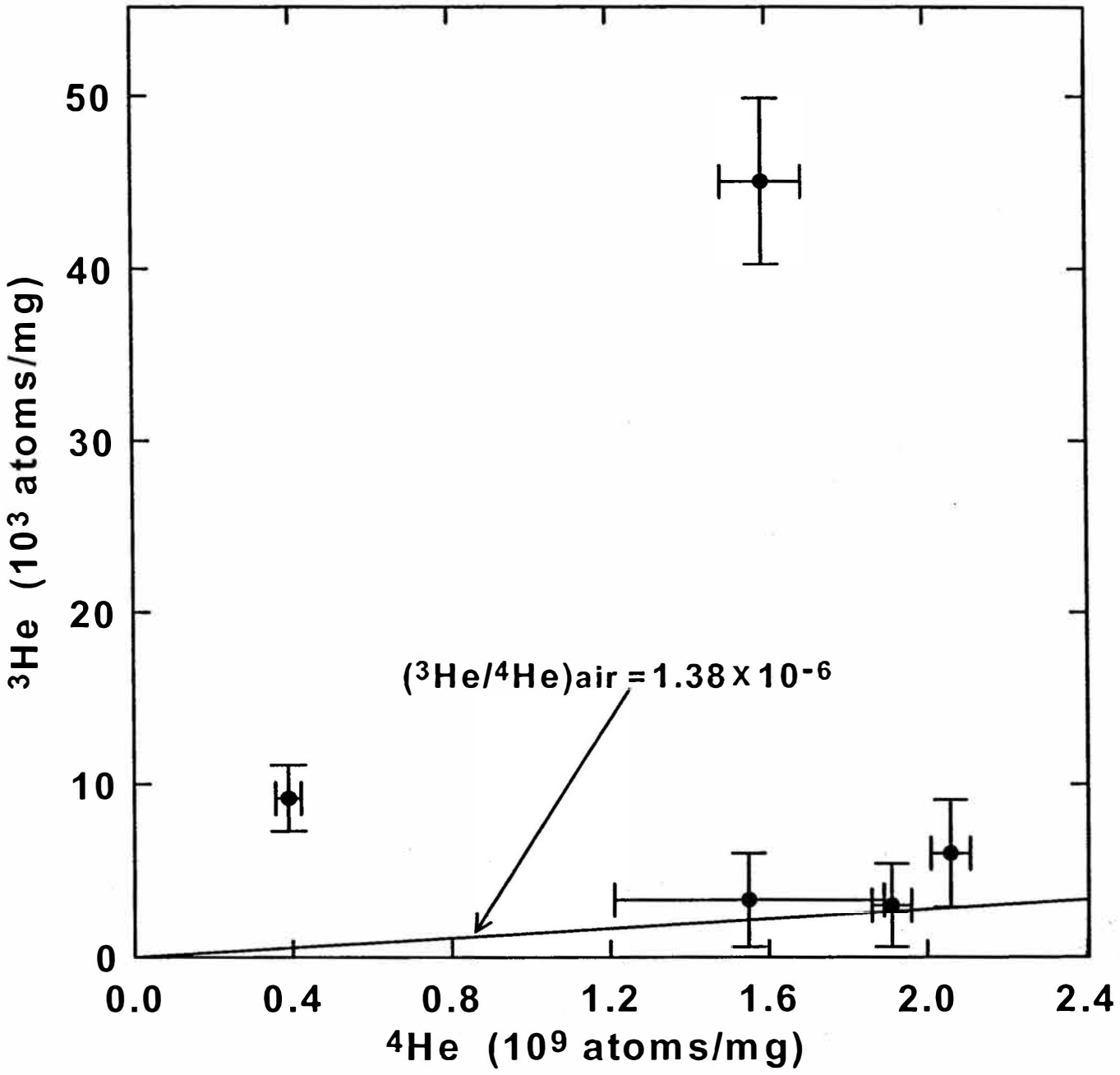

Figure 3. ^{3}He and ^{4}He concentrations in twelve samples of Pd-black.